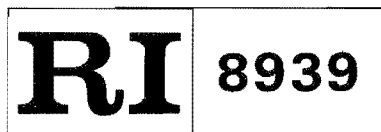


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# Assessment of Phosphogypsum as a Constituent of Aggregate Material

By A. May, J. R. Cobble, and J. W. Sweeney



UNITED STATES DEPARTMENT OF THE INTERIOR



**Report of Investigations 8939**

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**By A. May, J. R. Cobble, and J. W. Sweeney**



**UNITED STATES DEPARTMENT OF THE INTERIOR**

**Donald Paul Hodel, Secretary**

**BUREAU OF MINES**

**Robert C. Horton, Director**

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## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	in	inch
°C/h	degree Celsius per hour	pct	percent
°F	degree Fahrenheit	pcf	pound per cubic foot
ft	foot	psi	pound per square inch
g	gram	min	minute
g/mL	gram per milliliter	mm	millimeter
h	hour	yr	year

# ASSESSMENT OF PHOSPHOGYPSUM AS A CONSTITUENT OF AGGREGATE MATERIAL

By A. May,<sup>1</sup> J. R. Cobble,<sup>1</sup> and J. W. Sweeney<sup>2</sup>

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## ABSTRACT

Florida has accumulated about 400 million tons of phosphogypsum, a mineral process waste generated in the production of fertilizer, and is adding 30 million tons to this annually. To minimize storage of this waste and reduce potential environmental effects, the Bureau of Mines conducted research into utilizing the phosphogypsum, by identifying and developing high-volume uses for this material. Admixtures of phosphogypsum, fly ash, and lime that could produce a coarse aggregate suitable for road construction were investigated. Using phosphogypsum with asphalt, cement, cement-kiln dust, silica, clays, and oxychlorides to produce aggregate was also examined.

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## INTRODUCTION

The Bureau of Mines and the Florida Institute of Phosphate Research (FIPR) entered into an agreement to cofund research to develop a synthetic aggregate made from Florida phosphate industry waste materials, primarily phosphogypsum. The research addressed the mission of both agencies; from the Bureau's perspective, it investigated technology with wide generic application to economically utilize waste materials, and it met the FIPR objectives of developing technology to utilize phosphogypsum generated by the Florida phosphate industry.

The phosphate industry in Florida is a vital segment of the Nation's economy and provides a critical mineral required for fertilizer production. In 1983, the Bureau of Mines reported (1)<sup>3</sup> that Florida and North Carolina supplied 85 pct of the domestic and 28 pct of the world's phosphate requirements. About 82 pct of the Florida phosphate is converted into phosphoric acid, which is used to make fertilizers.

Phosphogypsum and gypsum are both calcium sulfate dihydrate. The name phosphogypsum is used to designate the by-product of wet-process phosphoric acid production, while gypsum refers to the natural mineral. Phosphate rock, which is composed of apatite minerals (calcium phosphates containing varying amounts of carbonate and fluoride), is digested with sulfuric acid and water to produce phosphoric acid, phosphogypsum, and minor quantities of hydrofluosilicic acid.

The Bureau reported in 1982 (2) that 335 million tons of phosphogypsum had accumulated in Florida and that phosphogypsum was being generated at a rate of about 33 million tons a year. By the year 2000, the projected accumulation will be over a billion tons of phosphogypsum.

In another Bureau study (3), baseline data were developed to assess the environmental impact associated with the storage of phosphogypsum, using the Environmental Protection Agency criteria (4-5).

In 1980, 19.5 million tons of gypsum was used in the United States for cement retarders, agricultural applications, fillers, plasters, and prefabricated products; this includes only 0.66 million tons of phosphogypsum, used in agriculture (1). Erlenstadt (6) discussed the use of phosphogypsum in cement retarders, fillers, plasters, and prefabricated products. Florida phosphogypsum contains traces of phosphate and fluoride, which must be removed in order to use the phosphogypsum in these applications. Wheelock (7) reported on the manufacture of sulfuric acid made from phosphogypsum. Another use for phosphogypsum is in road construction, especially with lime and fly ash. Fly ash has been extensively used as a construction material. Hester (8) gave construction and performance data for approximately 200 miles of concrete pavement containing a small amount of fly ash, which was constructed in south Alabama. The engineering properties, compositions, and performance of lime-fly ash mixtures were considered by Barenberg (9) and by the Transportation Research Board (10), in research sponsored by the American Association of State Highway and Transportation Officials in cooperation with the Federal Highway Administration. Minnick (11) mentioned the use of phosphogypsum with lime and fly ash in road construction but did not report details of its use. Brink (12) gave details on a 200-acre parking lot paved with compositions of lime, fly ash, and synthetic gypsum, containing about 20 pct synthetic gypsum. The synthetic gypsum resulted from the manufacture of hydrofluoric acid, from acid mine drainage sludge, and from sulfur dioxide scrubber sludge. No phosphogypsum was used in these applications.

<sup>3</sup>Underlined numbers in parentheses refer to items in the list of references at the end of this report.

This research investigated the development of a synthetic coarse aggregate composed of phosphogypsum, lime, and fly ash, which would be suitable for road construction. Such high-volume use of

phosphogypsum would reduce the storage problems associated with it. Its uses with asphalt, cement, cement-kiln dust, silica, clays, and oxychlorides were also investigated.

#### ACKNOWLEDGMENTS

The authors wish to acknowledge Dr. David P. Borris, executive director, FIPR, for his advice and assistance, and

also the Florida Department of Transportation for evaluating the synthetic phosphogypsum aggregate.

#### MATERIALS USED

The phosphogypsum used was a sample obtained from a USS Agri-Chemicals stockpile near Bartow, FL. The analysis and characteristics of Florida phosphogypsum have been fully described (2). The size distribution of phosphogypsum dried at 45° C is shown in figure 1. The scale used at the top of figure 1 was derived from the size openings of U.S. Standard sieves specified in the American Society for Testing and Materials (ASTM) standard method E 11-70 (13). The scale has the same form as plotting against log (size, millimeter) but has the advantages that the scale is linear, the units are small

integers, and the integers correspond exactly to the sieve numbers.

Two fly ash samples were used, one from Alabama and the other from Florida. The Alabama fly ash was from the Wilsonville, AL, steamplant and its production methods, quality control, and characteristics were presented by Styron (14). The Florida fly ash was from Tampa Electric Co.'s Big Bend powerplant. Analyses of these fly ashes are shown in table 1. A commercial high-calcium lime was also used.

TABLE 1. - Analyses of fly ash samples, percent

	Florida sample	Alabama sample
Component:		
SiO <sub>2</sub> .....	47.1	48.9
Fe <sub>2</sub> O <sub>3</sub> .....	24.2	14.9
Al <sub>2</sub> O <sub>3</sub> .....	16.3	23.8
CaO.....	4.1	3.1
MgO.....	.7	1.1
SO <sub>3</sub> .....	0	0
Water soluble.....	2.2	1.4
Moisture, weight loss at 110° C.....	.3	.3
Loss on ignition, weight loss at 750° C.....	1.6	1.9
Available alkali.....	.2	.3
Sieve analysis:		
Plus 30 mesh.....	.1	0
Plus 200 mesh.....	7.5	5.9
Minus 200 mesh.....	92.4	94.1

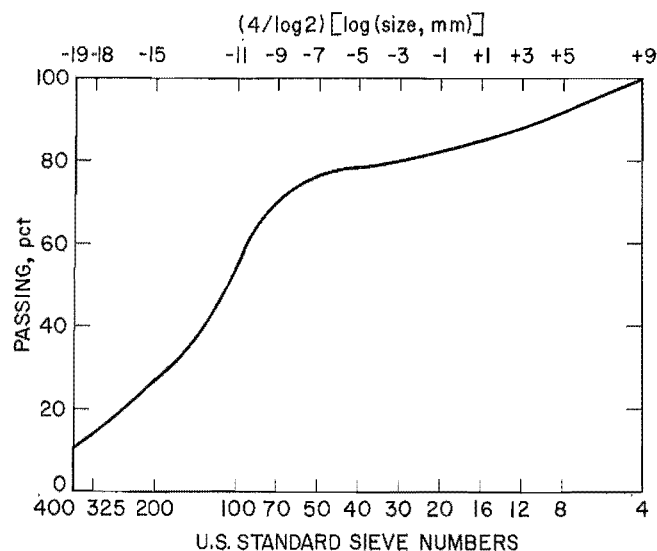


FIGURE 1. - Particle size distribution of phosphogypsum dried at 45° C.



Some tests were made using commercial ball clays, clay solids from phosphate rock beneficiation, cement-kiln dust, silica powder, grade AC-20 asphalt,

commercial calcium chloride, and reagent-grade calcium oxide, calcium hydroxide, and calcium chloride.

#### CRITERIA FOR EVALUATING SAMPLES

The criteria for evaluating samples of asphalt-concrete were free from ambiguity. The requirements, listed in the Florida Department of Transportation specifications (15), were applied to mixtures of phosphogypsum, sand, aggregate, and asphalt.

Requirements for aggregates are also listed in the Florida specifications. Tests such as the Los Angeles abrasion test are needed to evaluate compliance with the Florida Department of Transportation specifications, but such tests are not suitable for screening large numbers of compositions because of the quantities of materials needed. Therefore, unconfined compressive strength was used to evaluate the aggregate samples, because small samples sufficed and quantitative results were obtained that related to useful applications of aggregates. However, a specific value of compressive strength was needed as a criterion to indicate potentially useful products.

A study of 16 lime-fly ash pavements by the Transportation Research Board (10) gave the initial compressive strengths of the pozzolanic base materials and the strengths and performance evaluations of the pavements after 1 to 8 yr of service. The overall data indicated that an initial compressive strength of 1,000 psi, after curing for 7 days at 100° F,<sup>4</sup> gave

<sup>4</sup>This curing time is approximately equivalent to 28 days at 23° C. The lower temperature conditions were used for tests with phosphogypsum because they are standard for the ASTM procedure.

a high-quality pavement. Thus, a minimum strength of 1,000 psi was adopted in this investigation as the criterion by which to judge the phosphogypsum compositions. For comparison, the strength requirements of various mortars cured at 23° C and 95 pct relative humidity (R.H.) are shown in table 2.

TABLE 2. - Typical specifications for compressive strengths

Mortars	Compressive strength, 28-day, psi	ASTM specification
Pozzolans.....	600	C 593 (16)
Natural cement..	1,000	C 10 (17)
Blended hydraulic cement.....	1,200-3,500	C 595 (18)
Portland cement	3,200-4,000	C 150 (19)
Criterion adopted for this study.....	1,000	NAp

NAp Not applicable.

In addition to compressive strength, the expansion of compositions containing phosphogypsum is of vital importance. Standard specification ASTM C 33 (20) for concrete aggregate limits the expansion of concrete, made from 1 part job cement plus 2.25 parts aggregate, to 0.05 pct at 12 weeks or 0.10 pct at 6 months, when samples are exposed to saturated water vapor. The specification ASTM C 150 (19) for Portland cement limits the expansion of mortars exposed to sulfate and immersed in water to 0.045 pct in 14 days. In this investigation a maximum expansion of 0.05 pct was adopted for samples immersed in water for 12 weeks.

## COMPOSITIONS CONTAINING PHOSPHOGYPSUM

## ASPHALT-CONCRETE

Tests were performed to determine if phosphogypsum could be used to replace sand or fine aggregate in asphalt-concrete. Twenty mixes of various combinations of asphalt, phosphogypsum, sand, and coarse aggregate were tested.

The tests determined stability, resistance to plastic deformation, and flow of asphalt-concrete by the Marshall apparatus, ASTM standard method D 1559 (21). Also determined were bulk density, ASTM D 1188 (22), maximum specific gravity, ASTM D 2041 (23), and the percent air voids, ASTM D 3203 (24). The optimum asphalt content and the voids in the mineral filler were derived from the test data.

The supplement to the Florida Department of Transportation specifications (25) lists requirements for 12 types of

asphalt-concrete. There are four surface course mixes, S-I, S-II, Type II, and Type III; one patching mix, sand-asphalt hot mix, SAHM; three asphalt base course mixes, ABC-1, ABC-2, and ABC-3; and four wearing surface or friction course mixes, FC-1, FC-2, FC-3, and FC-4.

A mix containing 7.0 pct grade AC-20 asphalt and 93 pct mineral filler (composed of 20 pct phosphogypsum dried at 150° C, 30 pct sand, and 50 pct limerock aggregate) met the requirements for asphalt-concrete for Type III, SAHM, and ABC-1 mixes. Thus, phosphogypsum may be used as a mineral filler in asphalt-concrete mixes for surface or base courses or for patching. However, none of the mixes met the requirements for wearing or friction courses. Table 3 shows the test results for the 20-pct phosphogypsum mix and the requirements for Type III, SAHM, and ABC-1 mixes.

TABLE 3. - Asphalt-concrete containing phosphogypsum<sup>1</sup>

	Observed	Requirements <sup>2</sup>	
		Type III	SAHM and ABC-1
AGGREGATE SIZES, U.S. STANDARD SIEVE, PCT PASSING			
1/2 in.....	100.0	100	100
3/8 in.....	99.0	80-100	NAP
No. 4.....	72.5	65-100	NAP
No. 10.....	52.1	40- 75	NAP
No. 40.....	39.1	20- 45	NAP
No. 80.....	18.1	10- 30	NAP
No. 200.....	7.0	2- 10	0- 12
ASPHALT-CONCRETE TESTS			
Stability.....lb..	2,024	>1,000	>500
Flow.....0.01 in..	14	8-16	8-20
Voids in mineral aggregate.....pct..	20	>15	>15
Air voids.....pct..	5	5-12	5-16
Asphalt content...pct..	7	4.5-9	4-9
Unit weight.....psi..	142	NAP	NAP

NAP Not applicable. No requirements listed.

<sup>1</sup>Asphalt-concrete: 7 pct grade AC-20 asphalt, 93 pct aggregate. Aggregate: 20 pct phosphogypsum, 30 pct sand, 50 pct limerock stone.

<sup>2</sup>Florida Department of Transportation specifications (25).

The maximum amount of phosphogypsum that proved satisfactory was only 20 pct.<sup>5</sup> When higher percentages were tested, coating of all the aggregate particles with asphalt was incomplete, and the asphalt-concrete test results and the particle size distribution of the aggregate-phosphogypsum mixture did not meet specifications.

An asphalt-concrete Marshall test specimen was made using 7 pct grade AC-20 asphalt and 93 pct aggregate consisting of 50 pct sand and 50 pct synthetic aggregate, the latter replacing limestone. The synthetic aggregate was a hardened crushed composition containing 20 pct phosphogypsum, 13 pct lime, and 67 pct fly ash. When this specimen was immersed in water for 72 h, it showed excessive swelling and bleeding, which indicated that the synthetic aggregate was not suitable in asphalt-concrete.

#### CEMENT, CEMENT-KILN DUST, AND SILICA POWDER

Tests were performed to determine if the phosphogypsum could be used to replace sand in cement mortars or would produce strong, hard materials with cement-kiln dust or with silica powder. The mixtures with silica powder were used in attempts to reproduce claims in a patent by R. C. Vickery (26) that a building material, having compressive strengths of 3,000 to 5,000 psi, could be made from compositions of 1 to 25 pct siliceous material and 2 to 10 pct lime, with the remainder consisting of phosphogypsum.

Various mixtures of phosphogypsum, cement, cement-kiln dust, hemihydrate made from phosphogypsum, silica powder, lime, and water were made into standard 2-in

<sup>5</sup>The 20 pct refers to phosphogypsum dried at 150° C, the temperature normally used to dry aggregate in asphalt plants. Under these conditions phosphogypsum may dehydrate to the hemihydrate, and 20 pct of hemihydrate is equivalent to 23.7 pct of phosphogypsum.

cubes and tested by the ASTM method C 109 (27) for compressive strength. Typical results are shown in table 4. The compositions of the cement and the cement-kiln dust mixtures were the same as that of Portland cement mortar used in the standard compression test, but with phosphogypsum replacing sand and kiln dust replacing cement. The composition using silica powder was one listed in the patent cited. These compositions are shown in table 4.

TABLE 4. - Compressive strengths of cement, cement-kiln dust, and silica powder mixtures containing phosphogypsum, pounds per square inch

Age of test specimens, days	Phosphogypsum plus		Hemihydrate, lime, and silica powder <sup>3</sup>
	Kiln dust <sup>1</sup>	Cement <sup>2</sup>	
3.....	60	680	1,690
7.....	230	630	1,400
28.....	420	1,590	1,500

<sup>1</sup>65 pct phosphogypsum, 24 pct kiln dust, 11 pct water.

<sup>2</sup>65 pct phosphogypsum, 24 pct type 2 cement, 11 pct water.

<sup>3</sup>70 pct hemihydrate, 8 pct silica powder (325 mesh), 3 pct lime, 19 pct water.

To determine if an accelerated reaction would occur between phosphogypsum and cement or cement-kiln dust, 2-in cubes of the compositions shown in table 4 were autoclaved at 200° C and 225 psi for 16 h. The compressive strength of the cement mortar dropped to 290 psi and that of the cement-kiln dust mixture to 200 psi. The autoclave contained more water after the samples were treated than the amount initially placed in the autoclave. This indicated that the phosphogypsum had dehydrated to hemihydrate with the release of water hydration. Other mixes on autoclaving gave the same results--lowering of their strengths and release of water.

The strengths of the cement and silica powder compositions met the criterion, 1,000 psi, adopted for a useful aggregate. Cement-kiln dust compositions

failed this test. However, the strength of the cement-phosphogypsum mortar was less than half that required for Portland cement-sand mortars. Considering the relatively low strengths obtained, further investigations using cement, cement-kiln dust, or silica powders were terminated.

#### CALCIUM OXYCHLORIDES

The Bureau reported on applications of oxychlorides for refractories (28). The initial reaction to form these compounds occurs in minutes, followed by a slower reaction to form hard cementitious materials.

Numerous mixtures of reagent-grade calcium hydroxide, calcium chloride, and water were made to select a uniform procedure to produce oxychlorides. Of these mixtures, four were machined into cylinders, 1 in. in diam and 1 in high, for compression tests. The strengths of these samples averaged 2,200 psi. An oxychloride containing 20 pct phosphogypsum had a compressive strength of 2,100 psi.

Three different compositions, containing 10, 30, and 50 pct phosphogypsum and commercial lime and commercial calcium chloride, were investigated. All compositions had a 3:1 molar ratio of lime to calcium chloride. Four batches of each composition were made, and the samples were cast into molds 1.5 in. in diam by 1.5 in high. The samples were stored at approximately 25° C and 75 pct relative humidity until tested for their compressive strengths, which are shown in table 5. Each value in table 5 is the average of four batches.

The results showed that the strengths were very low and decreased with age and with increased phosphogypsum content. The samples prepared from both reagent-grade and commercial chemicals were also tested for their stability in water. The samples cracked and deteriorated extensively within several months.

TABLE 5. - Compressive strengths<sup>1</sup> of calcium oxychlorides<sup>2</sup> containing phosphogypsum, pounds per square inch

Phosphogypsum, pct	7 days <sup>3</sup>	28 days <sup>3</sup>	84 days <sup>3</sup>
10.....	450	416	NA
30.....	270	256	128
50.....	188	239	79

NA Not available. Samples cracked on curing.

<sup>1</sup>Averages of four batches of three samples per batch.

<sup>2</sup>Mols Ca(OH)<sub>2</sub>/mols CaCl<sub>2</sub> = 3.

<sup>3</sup>Curing time, at 23° C and 95 pct R.H.

Since the objective of this investigation was the practical development of an aggregate from phosphogypsum, the researchers did not investigate why commercial chemicals gave products whose strengths were so much lower than the strengths of the products obtained with reagent-grade chemicals. Because of the low strengths and the instability of the products in water, work on oxychlorides was discontinued.

#### CLAYS--FIRED SAMPLES

Briquettes, balls, and cylinders were prepared containing 25, 50, and 75 pct phosphogypsum, with the remainder either commercial ball clay or clay from phosphate rock beneficiation. A minimum amount of water was added to form a plastic mass. The briquettes were hand-formed in a mold 1.5 by 0.3 by 1 in. The balls were hand-formed to be about 0.5 to 0.75 in. in diam. The cylinders, 1 in. in diam by 1.3 in long, were formed in a press under 8,000 psi. All samples were dried at least 24 h before firing.

The briquettes and cylinders were placed in a cold furnace, brought up to 600°, 800°, or 1,000° C and kept at these temperatures 1 h, after which the furnace was turned off and the samples were allowed to cool in the furnace. The balls were placed in a hot furnace at 600°, 800°, or 1,000° C for 15 min and then removed. Some briquettes were heated to 1,300° C.

The briquettes were used to determine structural soundness visually and to measure dimensional stability. Samples were sound at 600°, 800°, and 1,000° C and disintegrated at 1,300° C, probably because gypsum decomposes at the higher temperature. The higher temperatures produced lighter colors and a gradual increase in shrinkage.

The balls were used to estimate the tolerances of the mixes to thermal shock. All samples remained intact when suddenly placed in the hot furnace as described. These specimens were hard and could be dropped from 10 ft on a hard surface with no damage.

The cylinders had small surface cracks but were used to measure the compressive strengths of the mixtures. These strengths are shown in table 6, which indicates that some of the fired mixtures may be suitable as an aggregate since they met the criteria of 1,000 psi compressive strength.

TABLE 6. - Compressive strengths of clay mixtures containing phosphogypsum--fired samples, pounds per square inch

Phospho- gypsum, pct	600° C <sup>1</sup>	800° C <sup>1</sup>	1,000° C <sup>1</sup>
COMMERCIAL BALL CLAY			
25.....	1,340	2,070	3,450
50.....	770	970	1,030
75.....	210	220	240
CLAY FROM PHOSPHATE ROCK BENEFICIATION			
25.....	610	1,260	2,790
50.....	280	410	1,050
75.....	90	90	210

<sup>1</sup>Firing temperature.

Further research on the fired samples was restricted to mixtures of clay from phosphate rock beneficiation and phosphogypsum, since both of these are byproducts of the phosphate industry. The work was directed toward eliminating the cracks and increasing the strengths of the cylinders. Standard mixing, forming, and firing techniques were used. Cracking continued to be a problem, even with cylinders 1.5 in. in diam and 0.5 in high, formed under 2,000-psi pressure and

heated at a rate of 50° C/h. After numerous tests, the cracking was reduced to surface flaws and the strength was greatly increased. Dimensionally stable cylinders were made having small shrinkages on firing and no measurable expansion when immersed in water.

The final method for making cylinders involved the addition of prefired grog to the clay-phosphogypsum mix and damp-pressing. The grog was made by firing clay and phosphogypsum to 1,000° C and crushing and screening the cooled material to minus 14 plus 35 mesh. The grog and the clay-phosphogypsum mix used for each cylinder had the same composition. This procedure reduced shrinkage and increased porosity. Based on the dry weight of clay plus phosphogypsum, 10 pct water was added and the moist mixture thoroughly blended and screened through a 28-mesh sieve. Then 15 pct grog was added, and cylinders were formed in a 1.25-in-diam die under 5,000 psi. The cylinders were dried overnight at 110° C and then heated at 200° C/h to the firing temperature of 1,050° C, which was maintained for 1 h. Results for two compositions made in this manner are shown in table 7.

#### FLY ASH AND LIME

As reported in the materials section, two fly ash samples were available. These were compared by measuring the strengths of mixtures containing 40 pct phosphogypsum, 10 pct lime, and 50 pct of the respective fly ash, on a dry basis, plus a minimum amount of water to form mortars. The average results are shown in table 8.

The strengths of the mixtures containing either fly ash would be adequate for aggregate. However, the remaining tests were made using the Florida fly ash because of its proximity to Florida phosphogypsum. Initially, compositions were investigated that contained 20 pct or more of phosphogypsum since the objective of the research was to find large-volume uses of phosphogypsum.

TABLE 7. - Phosphogypsum-clay compositions formed with 10 pct moisture and 15 pct grog

Tests	50 pct clay <sup>1</sup>	75 pct clay <sup>1</sup>
Dried, 110° C:		
Diameter.....in..	1.250	1.251
Height.....in..	0.855	0.851
Weight.....g..	33.75	33.68
Fired, 1,050° C:		
Diameter.....in..	1.233	1.250
Height.....in..	0.841	0.853
Weight.....g..	26.36	26.21
Suspended in water:		
Diameter.....in..	NAp	NAp
Height.....in..	NAp	NAp
Weight.....g..	16.63	16.37
Saturated with water, measured in air:		
Diameter.....in..	1.233	1.253
Height.....in..	0.841	0.853
Weight.....g..	33.03	33.47
Redried, 110° C:		
Diameter.....in..	1.234	1.248
Height.....in..	0.841	0.853
Weight.....g..	26.14	26.05
Leached <sup>2</sup> .....pct..	0.8	0.6
Compressive strength, psi:		
Fired at 1,050° C.....	1,950	4,080
Redried at 110° C <sup>3</sup> .....	1,960	4,150
Hardness when fired at 1,050° C..mos..	3.5	3.5
Absorption <sup>4</sup> .....pct..	25.3	27.7
Apparent porosity <sup>5</sup> .....pct..	40.7	42.5
Bulk density <sup>6</sup> .....g/mL..	1.6	1.5

NAp Not applicable.

<sup>1</sup>From phosphate rock beneficiation; balance phosphogypsum.

<sup>2</sup>(Fired weight - redried weight) (100)/fired weight.

<sup>3</sup>After 2 weeks immersion in water.

<sup>4</sup>(Saturated weight - fired weight) (100)/fired weight.

<sup>5</sup>(Saturated weight - fired weight) (100)/(saturated weight - suspended weight).

<sup>6</sup>Fired weight/(saturated weight - suspended weight).

TABLE 8. - Compressive strengths of Alabama and Florida fly ash compositions, pounds per square inch

Fly ash	7 days <sup>1</sup>	28 days <sup>1</sup>	84 days <sup>1</sup>
Alabama.....	180	1,180	2,800
Florida.....	310	2,080	3,700

<sup>1</sup>Curing time, at 23° C and 95 pct R.H.

#### Compressive Strength

A systematic investigation of the effects of various amounts of lime, fly ash, and phosphogypsum on the strengths of aggregate mixtures was undertaken.

Standard 2-in cubes of various compositions were tested by the ASTM method C 109 (27) for compressive strengths.

A series of tests was performed on mixtures with fly ash-lime ratios of 3:1, 5:1, and 10:1, each containing 20 to 80 pct phosphogypsum. Another series of tests was run on mixtures containing 35 pct phosphogypsum, 0 to 25 pct lime, and the remainder fly ash. Compressive strengths were determined on each specimen after curing for 7, 28, and 84 days at 23° C and 95 pct relative humidity.

TABLE 9. - Mixtures of fly ash-lime containing 20 to 80 pct phosphogypsum

Test	Components, dry basis, pct			Compressive strength at various curing times, <sup>1</sup> psi		
	Phosphogypsum	Lime	Fly ash	7 days	28 days	84 days
3:1 FLY ASH-LIME						
1.....	20	20.00	60.00	420	2,360	4,010
2.....	35	16.25	48.75	230	2,100	3,540
3.....	50	12.50	37.50	160	1,370	3,110
4.....	65	8.75	26.25	100	670	1,650
5.....	80	5.00	15.00	60	310	540
5:1 FLY ASH-LIME						
6.....	20	13.33	66.67	280	2,980	4,840
7.....	35	10.83	54.17	260	1,950	3,670
8.....	50	8.33	41.67	210	1,730	2,330
9.....	65	5.83	29.16	140	730	790
10.....	80	3.33	16.67	80	290	310
10:1 FLY ASH-LIME						
11.....	20	7.27	72.73	480	2,520	2,850
12.....	35	5.91	59.09	410	1,390	1,550
13.....	50	4.55	45.45	110	760	930
14.....	65	3.18	31.82	80	260	310
15.....	80	1.82	18.18	40	50	40

<sup>1</sup>At 23° C and 95 pct R.H.

Compressive strengths of the mixtures containing 20 to 80 pct phosphogypsum are given in table 9. Figures 2, 3, and 4 show the compressive strengths of the 3:1, 5:1, and 10:1 fly ash-lime mixtures, respectively. Results for all of these ratios show the same trends--an increase in strength with time and with a decrease in the phosphogypsum content.

The change in strength with time is indicated by the slopes of the lines in figures 2, 3, and 4. In figure 2, the slope is small between 28 and 84 days at 80 pct phosphogypsum; in figure 3, at 65 and 80 pct phosphogypsum; and in figure 4, at 35, 50, 65 and 80 pct phosphogypsum. These data indicated that only small changes in strength occurred after 28 days. Each of these "flat" lines represents a mixture having less than 6 pct lime.

The time for the mixtures to reach 1,000 psi is about the same for each fly ash-lime ratio for the same percent phosphogypsum. From the intersections of the lines with 1,000 psi on figures 2, 3, and 4, the times shown in table 10 were obtained. The curing time ranges from 2 to 7 weeks for compositions achieving greater than 1,000 psi.

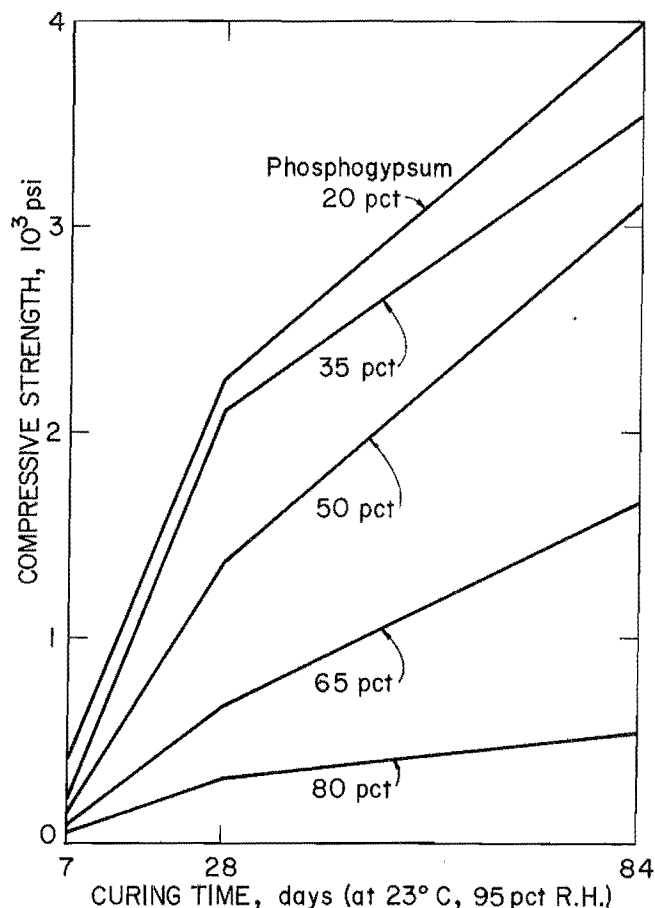


FIGURE 2. - Compressive strength versus time, 3:1 fly ash-lime ratio.

TABLE 10. - Times for fly ash-lime-phosphogypsum compositions to reach 1,000 psi

Phosphogypsum, pct	Average, <sup>1</sup> days
20.....	13
35.....	17
50.....	20
65.....	47
80.....	Nap

Nap Not applicable. Did not reach 1,000 psi.

<sup>1</sup>Averages for compositions whose strengths reached 1,000 psi.

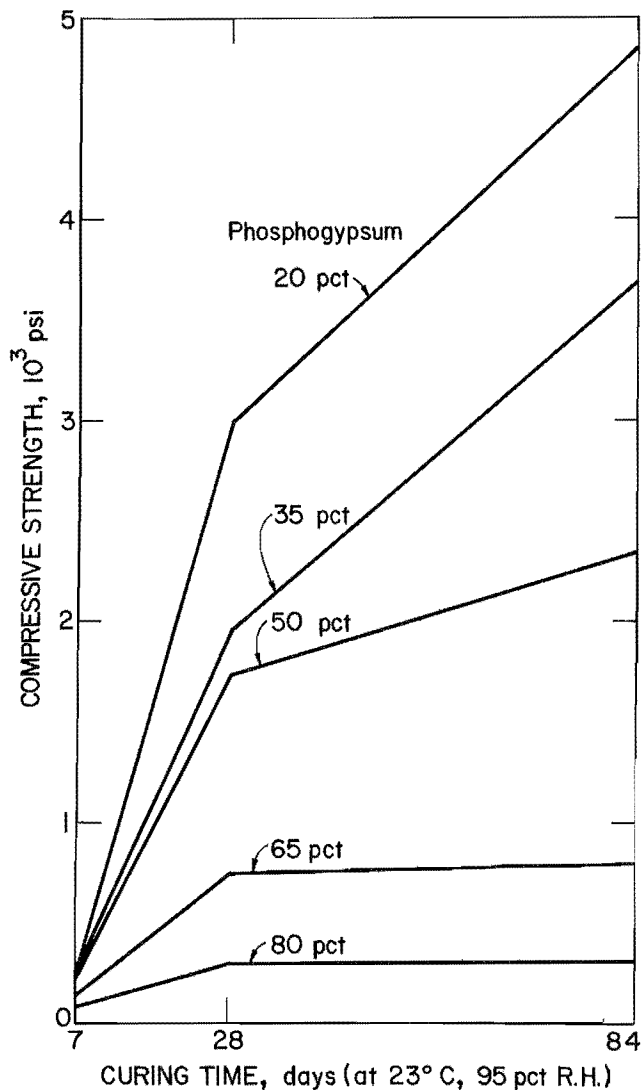


FIGURE 3. - Compressive strength versus time, 5:1 fly ash-lime ratio.

The change in compressive strength as a function of phosphogypsum, fly ash, and lime content is illustrated in figures 5, 6, and 7, respectively. These figures also indicate effects of fly ash-lime ratios.

The trends in compressive strengths appear to be well defined from figures 5, 6, and 7. For example, figure 5 shows almost a straight line from 20 to 65 pct phosphogypsum for the 5:1 fly ash-lime ratio. The correlation coefficient for this line is -0.998. However, the percent phosphogypsum, plus lime, plus fly ash, equals 100. These components are not independent variables. Higher phosphogypsum content necessarily requires lower lime and fly ash content. Thus, it is not certain if the lower strengths with increasing phosphogypsum content, shown in figure 5, were due to phosphogypsum, lime, or fly ash.

In an attempt to determine the relative importance of the ingredients, the method of linear multiple regression was applied

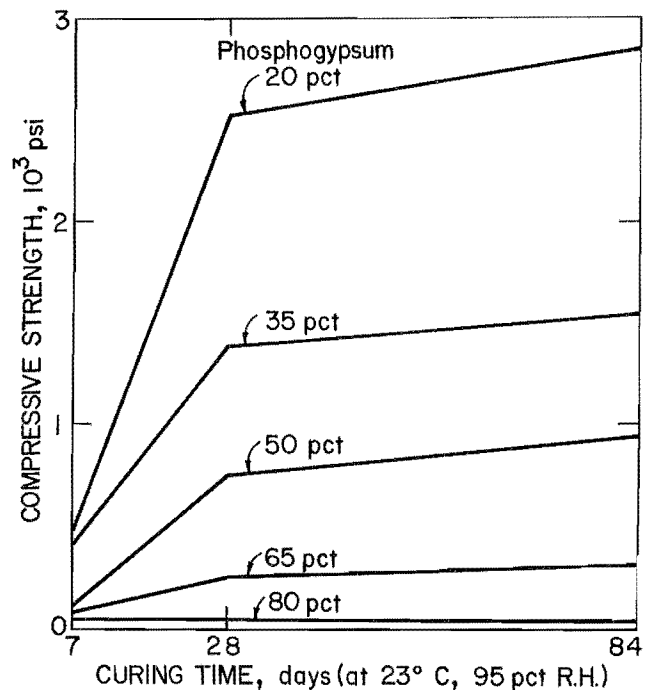


FIGURE 4. - Compressive strength versus time, 10:1 fly ash-lime ratio.



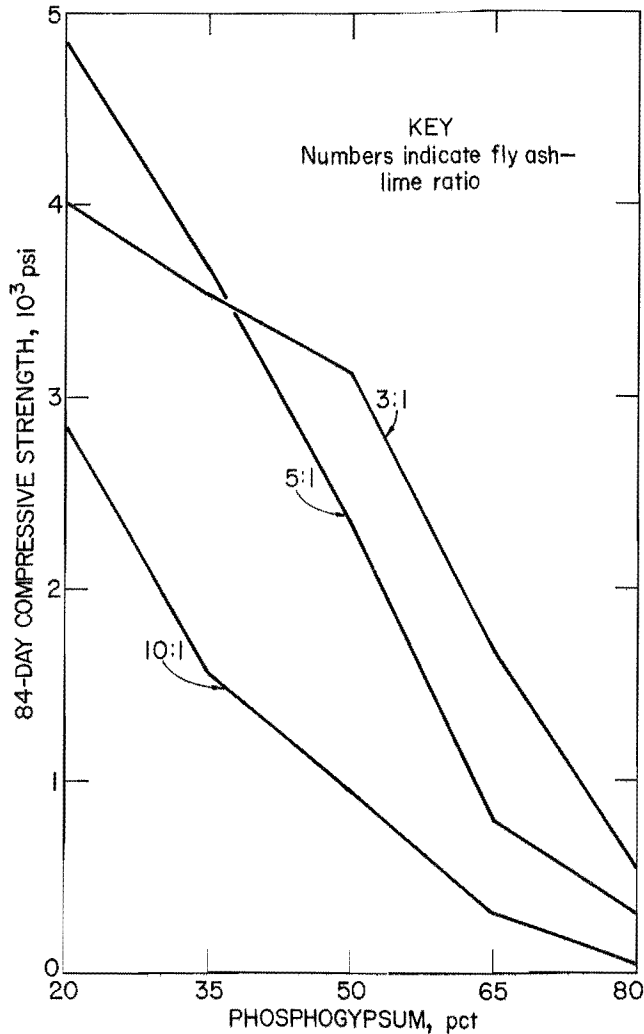


FIGURE 5. - Compressive strength versus 20 to 80 pct phosphogypsum.

to the 84-day strength data of table 9 to develop an equation:

$$S = a_0 + b_1L + b_2F + b_3G, \quad (1)$$

where  $S$  = compressive strength,

$L$  = percent lime,

$F$  = percent fly ash,

$G$  = percent phosphogypsum,

and  $a_0, b_1, b_2, b_3$  = coefficients determined from data treatment.

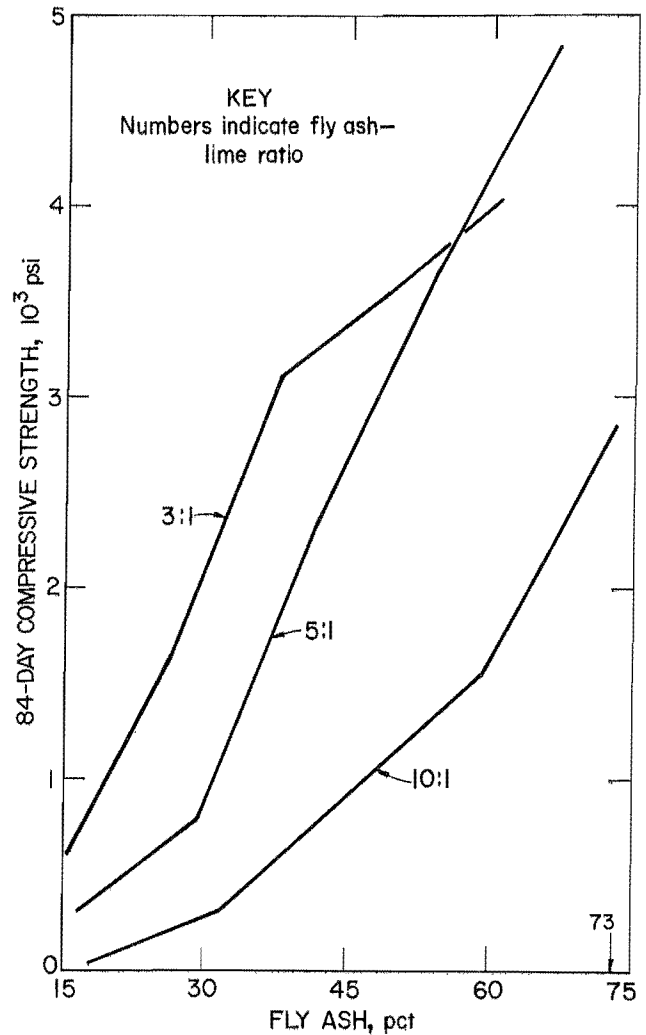


FIGURE 6. - Compressive strength versus percent fly ash.

Taking all the data at once, no unique solution to equation 1 was found. When various sets of data were fitted to equation 1, solutions of the equation were generated, but the standard errors in the coefficients were extremely large. However, when the compressive strength was considered as a function of percent lime, percent fly ash, or percent phosphogypsum:

$$S = a_1 + b_1L = a_2 + b_2F = a_3 + b_3G, \quad (2)$$

and the composition is given by equation 3:

$$F + L + G = 100, \quad (3)$$

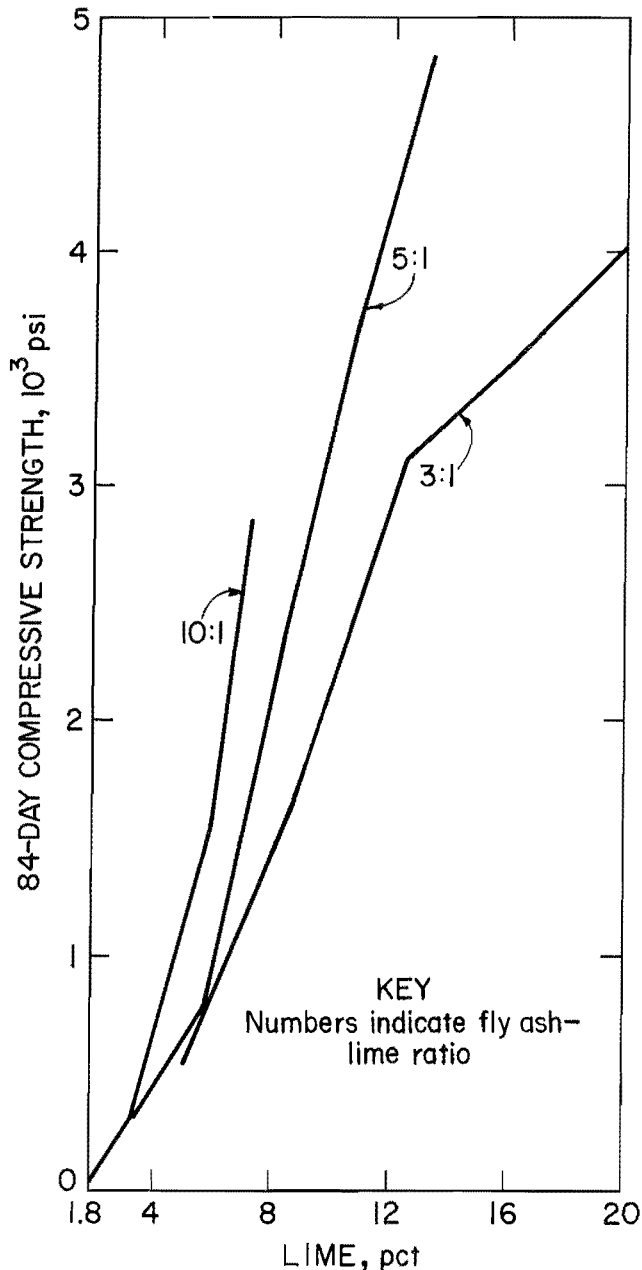


FIGURE 7. - Compressive strength versus percent lime.

the following relationships were derived:

$$b_2 = b_1 / (F/L), \quad (4)$$

$$b_3 = -b_1 / [(F/L) + 1], \quad (5)$$

$$a_2 = a_1, \quad (6)$$

and  $a_3 = a_1 - 100(b_3). \quad (7)$

The relative effects of lime, fly ash, and phosphogypsum are represented by  $b_1$ ,  $b_2$ , and  $b_3$ . Thus, from equations 4 and 5, for a 5:1 fly ash-lime ratio, the effect of lime is five times that of fly ash and six times that of phosphogypsum. Linear regression of the data confirmed the relationships derived in equations 4 through 7. Also, the standard errors of the coefficients were small. For example, for the 5:1 fly ash-lime ratio, there were standard errors of 132, 24, 5, and 4 psi in the calculated values of  $S$ ,  $b_1$ ,  $b_2$ , and  $b_3$ , respectively, and the correlation coefficient was 0.998.

To determine if the trends shown in figure 5 continued to 0 pct phosphogypsum, compressive strengths of 5:1 fly ash-lime mixtures with phosphogypsum contents from 0 to 15 pct were measured. Results are given in table 11. The trend did not continue to higher compressive strengths with lower phosphogypsum contents. This is shown by figure 8, which shows the 84-day compressive strengths for 5:1 fly ash-lime mixtures with phosphogypsum contents from 0 to 80 pct, from the data of tables 9 and 11. This figure shows that the phosphogypsum is not merely an inert "filler" but reacts with the lime and fly ash. Thus, phosphogypsum is an essential ingredient of these mixtures, indicating a possible high-volume use for it.

The 3:1, 5:1, and 10:1 fly ash-lime ratios gave different compressive strengths. To show how these ratios affected the strengths, they are compared in figure 9. The strengths are greatest for 20 pct phosphogypsum and least for the 80 pct phosphogypsum for all ratios. Figure 9 shows a distinctive feature of the data. The 20- and 35-pct-phosphogypsum mixtures increased in strength from the 3:1 to the 5:1 ratios while the 50-, 65-, and 80-pct-phosphogypsum mixtures decreased in strength.

TABLE 11. - Mixtures of 5:1 fly ash-lime containing 0 to 15 pct phosphogypsum

Test	Components, dry basis, pct			Compressive strength at various curing times, <sup>1</sup> psi	
	Phosphogypsum	Lime	Fly ash	28 days	84 days
17..	0	16.67	83.33	1,920	2,690
18..	5	15.83	79.17	2,870	3,530
19..	10	15.00	75.00	2,300	4,350
20..	15	14.17	70.83	1,630	4,700

<sup>1</sup>At 23° C and 95 pct R.H.

Compressive strengths, as a function of lime content, with a constant phosphogypsum content of 35 pct, are given in table 12 and figure 10. Figure 10 contains data from tables 9 and 12 and also indicates the fly ash-lime ratios. Maximum strength was obtained with a 5:1 fly ash-lime ratio and 10.8 pct lime. The

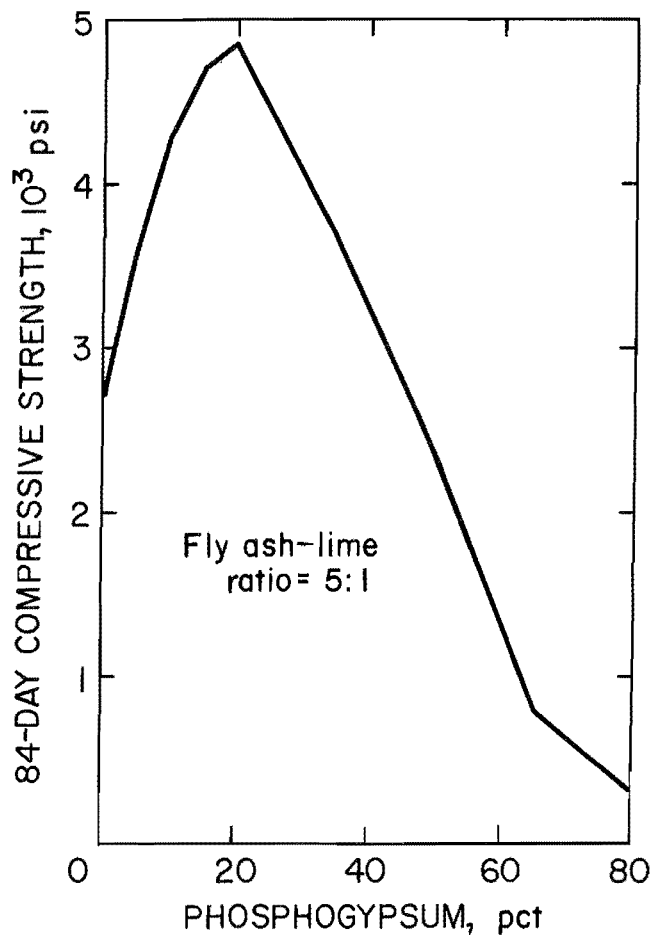


FIGURE 8. - Compressive strength versus 0 to 80 pct phosphogypsum.

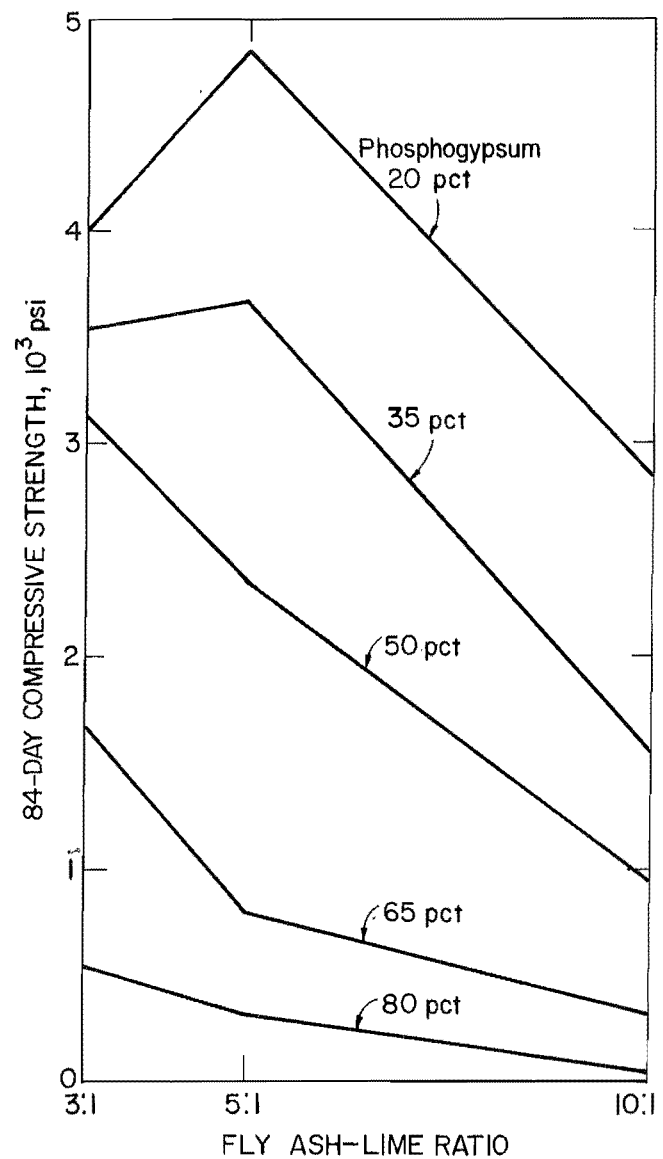


FIGURE 9. - Compressive strength versus fly ash-lime ratio.

TABLE 12. - Mixtures of 35 pct phosphogypsum containing 0 to 25 pct lime

Test	Components, dry basis, pct		Fly ash-lime ratio	Compressive strength at various curing times, <sup>1</sup> psi		
	Lime	Fly ash		7 days	28 days	84 days
21..	0	65	Nap	90	100	90
22..	5	60	12.00:1	190	660	760
23..	10	55	5.50:1	260	1,960	3,590
24..	15	50	3.33:1	250	1,940	3,550
25..	20	45	2.25:1	230	1,960	2,880
26..	25	40	1.60:1	400	2,280	3,180

Nap Not applicable.

<sup>1</sup>At 23° C and 95 pct R.H.

fly ash-lime ratio and percent lime for maximum strength differ from these values when the phosphogypsum content is different from 35 pct.

Figure 10 indicates that to develop adequate strength, the fly ash-lime ratio should be between 3 and 10 and the lime content should be between 6 and 11 pct. Mixtures containing more than 65 pct phosphogypsum would be excluded, since all samples with 65 pct or more phosphogypsum had low strengths. The range of compositions for adequate strength are shown in table 13.

TABLE 13. - Range of compositions of fly ash, lime, and phosphogypsum to produce aggregate strengths of 1,000 psi

	Range, pct
Phosphogypsum.....	0-65
Fly ash.....	33-60
Lime.....	6-11
Fly ash-lime ratio.....	3-10

A mixture containing 10 pct lime, 40 pct phosphogypsum, and 50 pct fly ash was tested for abrasion by the Los Angeles abrasion test. The loss was less than 50 pct, meeting the requirement of the Florida Department of Transportation specifications. Unit weight of the aggregate was 106 pcf, also meeting the specifications.

#### Expansion

The Bureau investigated the effects of various amounts of lime, fly ash, and phosphogypsum on the expansion of synthetic aggregate when immersed in water. A standard test method, "Potential expansion of Portland cement mortars exposed to sulfate," ASTM C 452 (29), was used, with modifications that were needed because of the nature of the samples. The standard method required the addition of gypsum to cement mortar to produce a 7.0 pct SO<sub>3</sub> content. The Bureau used 5, 20,

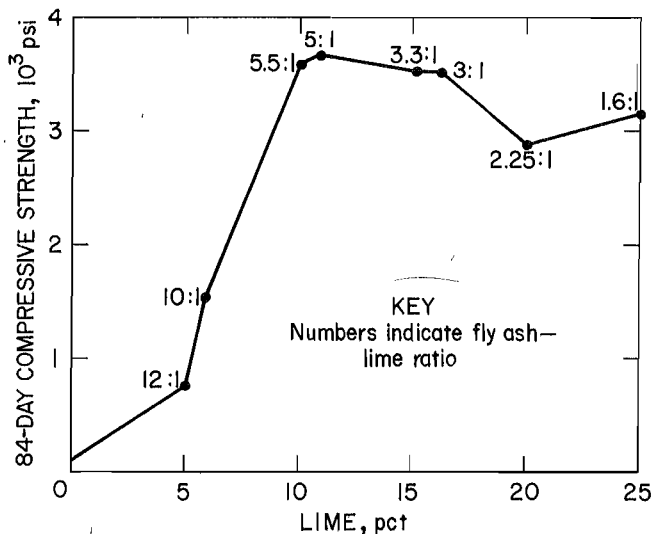


FIGURE 10. - Compressive strength versus percent lime, with 35 pct phosphogypsum.

35, and 50 pct phosphogypsum and 5, 10, 15, and 20 pct lime to determine the effects of each; the remainder of each composition was fly ash. These mixtures required a 2-week curing time to develop sufficient strength for the expansion measurements. The lengths of the test specimens were measured with a dial micrometer as required in the standard method. However, many of the samples expanded beyond the range of the micrometer. The lengths of these samples were measured with a machinist steel rule graduated in 1/64 in. The precision of the micrometer measurements was about 0.01 pct while that of the steel rule was about 0.16 pct.

The test specimens were immersed in water and their lengths were measured each week for 12 weeks. Then the specimens were air-dried 2 weeks, measured, immersed in water 2 weeks, and again measured. The cycle of drying and soaking in water was repeated as frequently as time permitted.

Table 14 shows the percent expansion of the samples at the end of the 12-week immersion period. All of the compositions greatly exceeded the criterion of 0.05 pct maximum expansion and thus would not be suitable for aggregate in cement-concrete in road construction. The data in table 14 also show that the expansion increased as the percent lime and the percent phosphogypsum increased.

TABLE 14. - Percent expansion of fly ash-lime-phosphogypsum samples<sup>1</sup> after immersion in water for 12 weeks

Phosphogypsum, pct..	5	20	35	50
5 pct lime.....	0.29	0.55	0.58	2.10
10 pct lime.....	.79	.97	2.43	NT
15 pct lime.....	.65	1.97	4.87	NT
20 pct lime.....	4.67	9.31	6.90	NT

NT Not tested. Cracked during immersion.

<sup>1</sup>Percent fly ash = 100, minus percent lime, minus percent phosphogypsum, dry basis.

All of the expansion data are shown graphically as plots of percent expansion versus time. Figure 11 shows the expansion of mixtures of 5 pct lime with 5, 20, 35, and 50 pct phosphogypsum. Only the 5-pct-lime mixture was tested with 50 pct phosphogypsum. With lime contents greater than 5 pct, the mixtures with 50 pct phosphogypsum cracked in water. Figures 12, 13, and 14 show results for 10, 15, and 20 pct lime, respectively.

Figures 11 through 14 show the data as measured, connected by straight lines. The inherent characteristics of the data can be most easily visualized by considering the results for 20 pct phosphogypsum (figs. 11-14). During the initial 12-week immersion in water, the time to reach constant percent expansion increased as the lime content increased. The percent expansion increased and then remained nearly constant after 2, 4, 6, and 10 weeks with 5, 10, 15, and 20 pct lime, respectively. Following the 12 weeks of water immersion, the samples shrank on drying and expanded again on soaking in water. The 5-, 35-, and 50-pct-phosphogypsum compositions changed their dimensions in the same manner as the 20-pct-phosphogypsum composition.

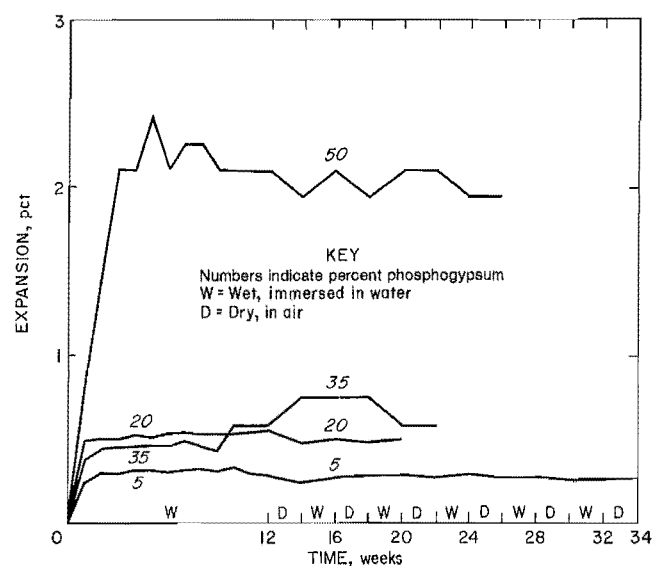


FIGURE 11. - Expansion, 5-pct-lime mixtures.

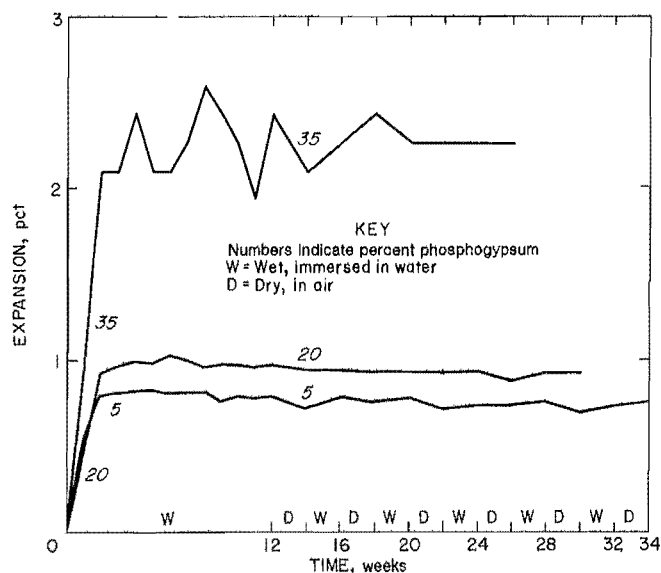


FIGURE 12. - Expansion, 10-pct-lime mixtures.

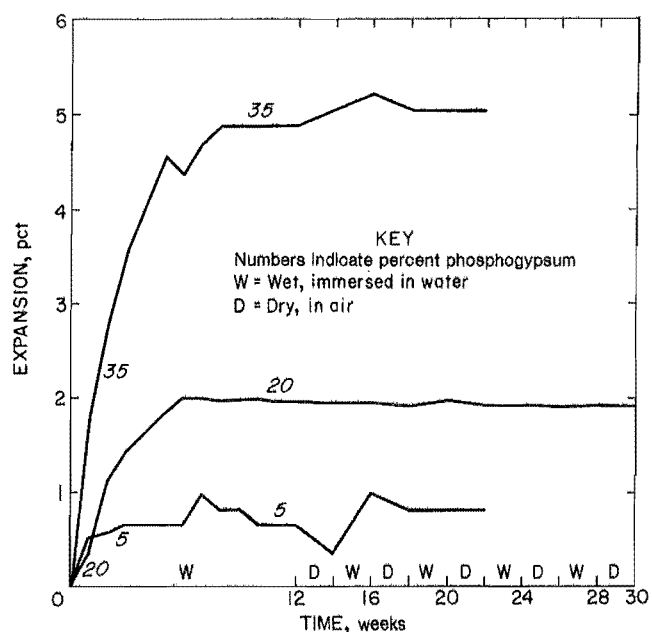


FIGURE 13. - Expansion, 15-pct-lime mixtures.

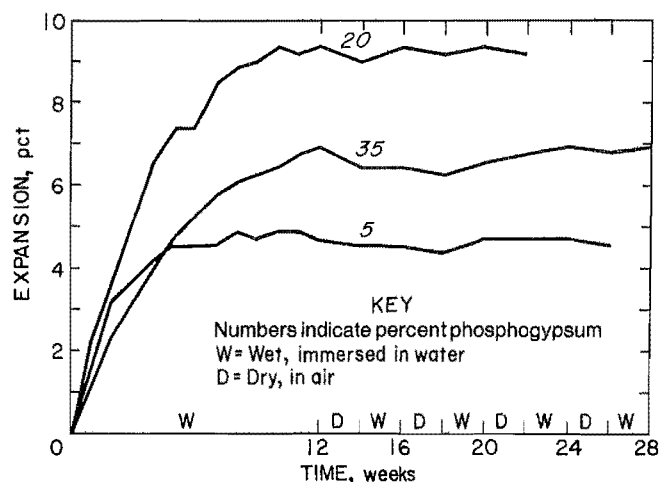


FIGURE 14. - Expansion, 20-pct-lime mixtures.

The precision of the results can be estimated from the variability of the data during the initial 12 weeks of immersion, after the expansions leveled off. This gave standard errors of 0.06 pct for expansions less than 2 pct and 0.15 pct for expansion greater than 2 pct.

In addition to the magnitude of the initial expansions, given in table 14, the Bureau was concerned with the dimensional stability of the samples after this expansion. This stability would indicate the possible application of these mixtures to construction purposes on a long-time basis with varying moisture conditions. Figures 11 through 14 show that the changes in expansion after 12 weeks were much smaller than the initial expansions. Table 15 shows the test results for the samples after the drying and soaking cycles.

TABLE 15. - Expansion test results for fly ash-lime-phosphogypsum samples<sup>1</sup> after drying and soaking cycles

Phosphogypsum, pct.....	5	20	35	50
WEEKS TESTED <sup>2</sup>				
5 pct lime.....	22	8	10	14
10 pct lime....	22	18	14	NT
15 pct lime....	10	18	10	NT
20 pct lime....	14	10	16	NT
PERCENT EXPANSION <sup>3</sup>				
5 pct lime.....	-0.02	-0.05	0	0.16
10 pct lime....	-.03	-.04	-.17	NT
15 pct lime....	.16	-.07	.17	NT
20 pct lime....	-.15	-.17	0	NT
STANDARD DEVIATION <sup>4</sup>				
5 pct lime.....	0.01	0.01	0.09	0.08
10 pct lime....	.03	.02	.10	NT
15 pct lime....	.12	.02	.07	NT
20 pct lime....	.12	.14	.25	NT

NT Not tested. Cracked during immersion.

<sup>1</sup>Percent fly ash = 100, minus percent lime, minus percent phosphogypsum, dry basis.

<sup>2</sup>After 12 weeks immersion; tested in cycles of 2 weeks drying and 2 weeks soaking in water.

<sup>3</sup>Final percent expansion minus percent expansion at 12 weeks.

<sup>4</sup>Standard deviation of expansion measurements after 12 weeks.

The expansion percents given in table 15 were the final expansion measurements minus those at 12 weeks. The final expansion and that at the end of the 12-week immersion could have coincidentally agreed and not accurately reflected the changes after the initial 12-week immersion. The standard deviations<sup>6</sup> of the expansion after the 12-week immersion more accurately reflect the changes that occurred. These are also given in

table 15. Both sets of data--the percent expansion and the standard deviations--show that the expansions were small after the initial immersion period.

The initial 12-week expansion data was fitted to equation 8:

$$Y = \frac{x}{a + bx}, \quad (8)$$

where  $x$  = weeks expansion,

$Y$  = percent expansion,

and  $a$  and  $b$  = constants derived from regression analysis to fit the data to equation 8.

The results of equation 8 showed excellent correlation with the data. The maximum expansion occurs when  $x$  is large, and this maximum equals  $1/b$ . The average error was 0.06 pct for expansions less than 2 pct and 0.213 pct for expansion greater than 2 pct. Thus, equation 8 represents the data almost within the experimental error.

Equation 8 was based on the initial 12-week expansion. Application of equation 8 to the data after the initial 12-week immersion gave results that were essentially linear, with the errors averaging 0.003 pct less than the standard deviations given in table 15.

<sup>6</sup>The standard deviations of the differences between the final percent expansions minus the percent expansions at 12 weeks are numerically identical to the standard deviations of the percent expansions.

## SUMMARY AND CONCLUSIONS

This investigation showed that using phosphogypsum with silica powder or calcium oxychlorides to make aggregates is not practical. The products obtained had low strengths or stability.

Phosphogypsum may be used as a mineral filler in asphalt-concrete. Asphalt-concrete containing 7 pct grade AC-20 asphalt and 93 pct aggregate (consisting of 20 pct phosphogypsum, 30 pct sand, and 50 pct limerock stone) met the Florida Department of Transportation specifications (25) for Marshall stability for Type III, SAHM, and ABC-1 asphalt-concrete. As a mineral filler, and not a constituent of an aggregate, only about 20 pct phosphogypsum can be used in asphalt-concrete because its particle size is too small to replace all the fine aggregate in these mixtures.

Mixtures containing 25 and 50 pct phosphogypsum and the remainder clay from phosphate rock beneficiation produced aggregate when fired at 1,000° C for 1 h. The compressive strengths exceeded 4,000 psi. The cost of firing the mixes may be a detriment to this use. However, clays from phosphate beneficiation and phosphogypsum are both waste products of the phosphate industry, and both could be utilized in this application.

Coarse aggregate made from mixtures of lime, fly ash, and phosphogypsum obtained maximum compressive strengths of 4,800 psi, requiring no energy other than mixing. These mixtures may contain as much as 50 pct phosphogypsum. However, they are slow curing, requiring from 2 to 7 weeks to reach a strength of 1,000 psi and about 3 months to develop higher strengths.

The strengths decreased with an increase in phosphogypsum content and increased with an increase in fly ash content. For adequate strength, the lime content should be about 6 to 11 pct. Below 6 pct lime, strengths are low, and above 11 pct lime, strengths remain about the same. The fly ash-lime ratios may vary from 3:1 to 10:1. Mixtures containing a maximum of 50 pct phosphogypsum, 6 to 10 pct lime, a 3:1 to 10:1 fly ash-lime ratio, and a minimum of 38 pct fly ash produced aggregate with 28-day compressive strengths exceeding 1,000 psi. Expansion of these mixtures in water was a maximum of 9 pct. The swelling characteristics of the lime, fly ash, and phosphogypsum compositions may limit the use of these mixtures.

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